

A Multiscale Approach to Determination of Thermal Properties and Changes in Free Energy: Application to Reconstruction of Dislocations in Silicon

T.D. Engeness and T.A. Arias

Department of Physics

Massachusetts Institute of Technology Cambridge, MA 02139

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Abstract

We introduce an approach to exploit the existence of multiple levels of description of a physical system to radically accelerate the determination of thermodynamic quantities. We first give a proof of principle of the method using two empirical interatomic potential functions. We then apply the technique to feed information from an interatomic potential into otherwise inaccessible quantum mechanical tight-binding calculations of the reconstruction of partial dislocations in silicon at finite temperature. With this approach, comprehensive *ab initio* studies at finite temperature will now be possible.

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Our understanding of the detailed processes underlying the behavior of condensed matter systems has progressed tremendously over the last fifteen years. Electronic structure techniques give insight into the electronic origins of phenomena, but most readily for fixed lattices at zero temperature. Modern simple, but realistic, interatomic potentials reveal the lattice processes underlying complex phenomena at finite temperature. One of the greatest challenges in condensed matter theory is to understand the electronic origins of solid state phenomena at finite temperature. Comparatively little progress has been made to date in this area because of the tremendous complexity of combining the large number of degrees of freedom needed to describe the electrons with the large number of ionic positions needed to describe the occupied regions of the lattice phase space at finite temperature. In this letter we show that there is an exact separation of the finite-temperature electronic-structure problem into two far simpler parts, a finite-temperature lattice part, which may be studied using approximate coarse-grained lattice models, and

the electronic structure part, which may be studied using highly accurate, fine-grained calculations.

Empirical interatomic potentials do not treat the electronic degrees of freedom explicitly, but have proved successful in modeling the general behavior of materials ranging from insulators [1] through semiconductors [2, 3] and metals [4]. These models capture basic interatomic behavior and their simplicity makes them well suited for the evaluation of thermal averages. However, because empirical models coarse-grain over the electronic degrees of freedom, they generally do not provide sufficiently accurate information for quantitative predictive studies.

Tight-binding models represent a next step in detail of description and reliability. These models include the electrons explicitly, but restrict their wave functions to linear combinations of atomic orbitals [5, 6, 7]. These potentials are therefore applicable over a wider range of phase space than interatomic potentials and provide certain electronic information. Tight-binding calculations are far more demanding than their empirical interatomic counterparts. Direct Monte Carlo or molecular dynamics calculations of systems at finite temperature are sufficiently demanding that the development of specialized approximate techniques is an active area of research [8].

Ab initio calculations attempt to describe all relevant electronic degrees of freedom. They give a good description of the physics of condensed matter systems over a wide range of phase space [9]. At present, density functional based calculations represent the greatest level of detail at which extended crystalline defects may be studied. Because the calculation of thermal averages with Monte Carlo or molecular dynamics methods requires the evaluation of many configurations to sample phase space fully, *ab initio* calculations of thermal properties such as free energy

differences [10] are tremendously demanding and infrequently attempted.

Finite temperature studies require a strategy for obtaining a proper ensemble. In general, the populated regions of phase space consist of a very narrow surface. To explore this surface with uniform sampling is impossible for a complex system because the surface occupies such a miniscule volume of phase space. As an alternative, one may start from a point on the occupied surface and then make small steps to explore it. One then always explores relatively relevant points in phase space, but covering the entire surface then requires an enormous number of steps. This can be manifested as correlation between large numbers of consecutive samples or as becoming trapped in local energy minima. This small-step approach is the essence of the two standard methods for evaluation of thermal averages: molecular dynamics [11] and Monte Carlo calculations based on the Metropolis algorithm [12].

As an alternative, we propose to separate the problem into two parts. First, we fully explore the relevant regions of phase space using a coarse-grained Hamiltonian, such as an interatomic potential for which extensive calculations based upon one of the traditional small-step approaches are tractable. Once the relevant regions are identified, we evaluate physical observables within the target fine-grained Hamiltonian, which may include electronic information, and combine the results to obtain proper averages over the fine-grained ensemble. Below we demonstrate that modern interatomic potentials are sufficiently close to their *ab initio* counterparts that thermal averages may be computed to within the accuracy of density functional theory by performing *ab initio* calculations on a very limited number of samples drawn from the interatomic ensemble. Our approach takes optimal advantage of the radical separation in computational time scales which interatomic potentials and quantum mechanical calculations exhibit. Rather than employing *ad hoc* non-physical Hamiltonians in a spirit similar to umbrella sampling [13], we propose the use of physical, albeit coarse-grained, Hamiltonians.

Corrected Ensemble Averages — The first phase of our approach is to run a large-scale exploration of phase space with a simplified model, using an appropriate, traditional thermodynamic approach. Drawing samples from the resulting configurations allows the more demanding model to be applied to truly uncorrelated, properly distributed points in phase space. So long as the two Hamiltonians are sufficiently correlated, we are assured that the samples

selected are physically relevant to ensemble averages over the fine-grained Hamiltonian.

To correct for the differences in the thermal distributions of the two Hamiltonians, each sample i selected from the initial simulation must be weighted by its relative probability in the two ensembles, the *corrective Boltzmann factor*

$$B_i^{f \leftarrow c} = \exp \left[-\beta(\mathcal{H}_i^f - \mathcal{H}_i^c) \right]. \quad (1)$$

Here, β is the inverse temperature, and \mathcal{H}_i^c and \mathcal{H}_i^f are the energy of configuration i within the coarse-grained and fine-grained models, respectively. Once given the corrective Boltzmann factors, the average of any observable \mathcal{O} in the ensemble of \mathcal{H}^f is

$$\langle \mathcal{O} \rangle_f = \frac{\sum_i B_i^{f \leftarrow c} \mathcal{O}_i}{\sum_i B_i^{f \leftarrow c}}. \quad (2)$$

Free energies — One common approach to the calculation of free energies is thermodynamic integration [14], which gives the free energy difference between two macrostates characterized by the parameter values $\lambda = 0$ and $\lambda = 1$ as $\Delta F = \int_0^1 \langle \frac{\partial E}{\partial \lambda} \rangle_\lambda d\lambda$, where the average is computed over the Boltzmann distribution at fixed λ . In practice, the integral is computed numerically by sampling a finite number of values of λ . When λ is a generalized coordinate, ΔF is the integral of the thermal average of the corresponding generalized force.

Proof of Principle — To demonstrate the soundness of this approach we use two potentials which are sufficiently simple to allow direct comparisons using brute-force techniques. We have chosen two models which differ from each other at least as much as typical interatomic potentials differ from density functional calculations. This allows us to address the issue of whether or not empirical potentials yield distributions sufficiently close to *ab initio* distributions that (2) may be evaluated reliably using a tractable number of samples.

To play the role of the coarse-grained Hamiltonian \mathcal{H}^c , we have chosen an early version of an interatomic potential for silicon which is still under development. The Stillinger-Weber model [2] plays the role of the fine-grained Hamiltonian \mathcal{H}^f . The standard deviation in energy differences $\mathcal{H}_f - \mathcal{H}_c$ over thermally distributed samples provides a useful measure of the inter-Hamiltonian discrepancy. We found that, for the system we study below, this measure is the same (to within ten percent) for our two interatomic potentials as it is for the Stillinger-Weber potential and density-functional calculations. Later we shall apply

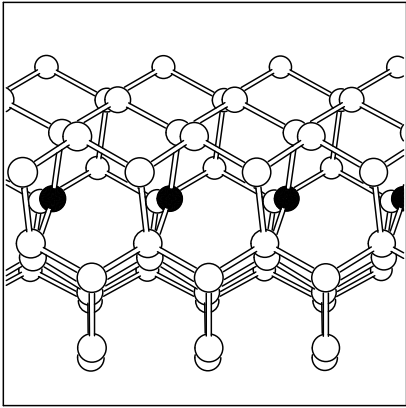


Figure 1: Unreconstructed ($\lambda = 1$) configuration of the 30° partial dislocation (glide set) in silicon. Atoms in black are core atoms which bond together in pairs upon reconstruction.

this measure to determine the relative suitability of different interatomic potentials in our procedure.

The physical system to which we apply our method is the 30° partial dislocation (glide set) in silicon. Figure 1 shows the core of this dislocation in the unreconstructed state. In nature, the core atoms indicated in black in the figure move together in a period-doubling reconstruction to form dimers which saturate all dangling bonds and thereby minimize the energy of the dislocation. To illustrate our approach, we calculate the free energy of this reconstruction at $T = 930\text{K}$, where some indirect experimental information is available [15, 16]. We use a periodic supercell of 96 atoms containing a dislocation-antidislocation core at a separation of 14\AA .

Figure 2 shows the cumulative changes in free energy for \mathcal{H}^c and \mathcal{H}^f (dashed and solid lines, respectively) as a function of λ as we drive the dislocation core from its reconstructed ($\lambda = 0$) to its unreconstructed ($\lambda = 1$) state. The figure also shows the statistical uncertainties remaining after the evaluation of twenty-five and fifteen *million* samples for \mathcal{H}^c and \mathcal{H}^f , respectively. As the figure illustrates, this number of samples is necessary to produce a reliable estimate of the final free energy difference within the Metropolis algorithm. Note that the final free energy change under \mathcal{H}^c is much lower than for \mathcal{H}^f and that the energy profile for \mathcal{H}^c exhibits extraneous local minima and maxima. The challenge to our multiscale method is to correct for the far lower free energy and spurious local minima and maxima of \mathcal{H}^c while using the *same* samples which led to the distorted curve for

\mathcal{H}^c .

The dash-dotted line Figure 2 displays the results we obtain with the multiscale approach. To produce these results, we first made five separate runs each drawing only one *thousand* independent samples at large intervals from the direct simulation under \mathcal{H}^c . We then evaluate the generalized force using \mathcal{H}^f and compute the average force at each value of λ for each run according to (2). Finally, we find the mean and standard deviation among the forces of the five runs at each λ and integrate the results numerically to give the free energy curve and uncertainties that appear in the figure. The fact that the newer curve has quite similar statistical uncertainties to the previous curves while computed from three orders of magnitude fewer samples underscores the fact that the vast majority of samples in the brute-force Metropolis approach only serve to generate the Boltzmann distribution but do not contribute significantly independent statistical information to the averages. If a sampling scheme better than the Metropolis algorithm were employed, the comparison would be less favorable for our approach. However, we note that our approach is direct, efficient and as general as the availability of suitable atomistic potentials. Figure 2 also shows that the averaging procedure (2) succeeds in eradicating the spurious maxima and minima of the coarse-grained Hamiltonian. The final free energy of reconstruction determined using the multiscale approach is 0.711 ± 0.019 eV, in good agreement with the result of the brute-force method, 0.712 ± 0.010 eV. We thus see that the low free energy difference under \mathcal{H}^c is indeed properly compensated, even when working with a radically reduced number of samples.

To obtain a statistical uncertainty in the free energy difference of 0.043 eV, which is within the accuracy of the best density functionals [17], the preceding calculation could be done with a single run, instead of five. This would require the evaluation of a total of only *one thousand* samples, quite feasible for *ab initio* work.

While it is true that the corrective factors fluctuate exponentially with the *total* energy discrepancy $\mathcal{H}_f - \mathcal{H}_c$, whose standard deviation scales as the square root of the number of atoms in the system, the corrected average (2) does not fluctuate among runs nearly as widely. This is because (2) is a weighted average of the observable \mathcal{O} , and, therefore, the fluctuations of \mathcal{O} place an absolute upper bound on the fluctuations of (2). The system size dependence of the fluctuations of (2) thus ultimately becomes the system size dependence of the fluctuations of \mathcal{O} . If \mathcal{O} is a local or intensive parameter, as we have here,

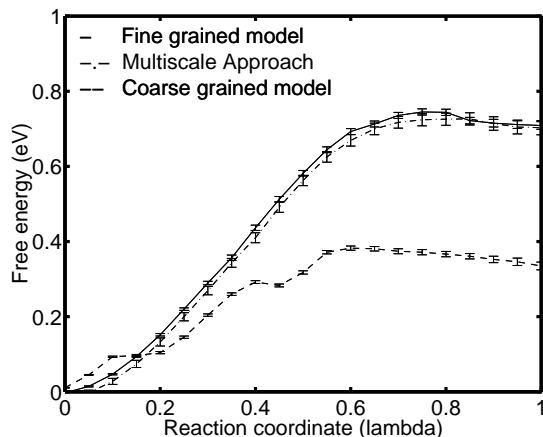


Figure 2: Free energy of the silicon 30° partial dislocation (glide set) as driven from its reconstructed ($\lambda = 0$) to its unreconstructed ($\lambda = 1$) state.

these fluctuations do not increase with system size.

For runs of fixed length, increases in fluctuations in the corrective factors result in fewer values of \mathcal{O} contributing to the final average. It thus becomes more difficult to detect the correlation between the observable and the inter-Hamiltonian discrepancy. However, *local* observables, such as our generalized force, are largely uncorrelated with the *global* energy discrepancy. When these quantities are completely uncorrelated, (2) reduces to $\langle \mathcal{O} \rangle_f = (1/N) \sum_i \mathcal{O}_i$. This direct average yields a free energy of reconstruction of 0.682 ± 0.008 eV, in excellent agreement with the exact result. The correlation between the generalized force and the energy discrepancy thus corresponds to the remaining 0.02 to 0.04 eV in the free energy, which the corrective Boltzmann factors capture rather well within our present run length and system size. Numerical experiments on model random variables reveal that, for a fixed run length, the effect of correlation between a local observable and the energy discrepancy degrades slowly with system size, approximately as the square root of the number of atoms. As the present scale of one hundred atoms approaches the maximum size feasible for current *ab initio* calculations with extensive exploration of phase space, we do not expect this degradation to present a significant problem for some time. Much can be done on the scale of one hundred atoms with our approach in its present formulation.

Multiscale model of dislocation cores at finite temperature — As a first truly multiscale application of our approach, we shall now demonstrate the use of

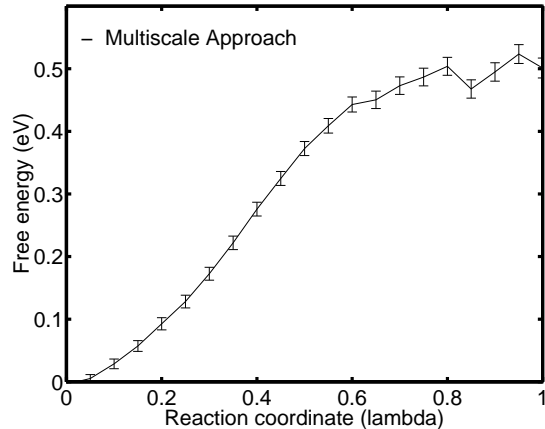


Figure 3: Multiscale calculation of quantum mechanical free energy of reconstruction

interatomic potential functions, which do not deal explicitly with electronic degrees of freedom, to generate samples for quantum-based tight-binding calculations, which do. The traditional Monte Carlo approach would demand the evaluation of millions of tight-binding configurations, requiring years of computing time.

For the present calculations, we use the tight-binding Hamiltonian of Sawada [6] with the modifications proposed by Kohyama [7]. This model provides a relatively good description of the bulk, dimer and surface energetics of silicon. A limited number (about fifty) of preliminary runs on our target system shows that the standard deviation in energy discrepancy between this tight-binding model and the two interatomic potentials are 0.40 ± 0.04 eV and 0.57 ± 0.07 eV, with the Stillinger-Weber yielding the lower value. Accordingly, we use the Stillinger-Weber potential to explore the phase space of our system.

Figure 3 presents the quantum mechanical tight-binding free energy profile of reconstruction calculated with the multiscale approach. Our results are based on the energy and forces of only twelve *hundred* samples drawn from the Stillinger-Weber potential. With the traditional Monte Carlo approach, a run of such length would produce at most a few independent points in phase space, while our calculation represents an extended exploration of the canonical distribution. Our tight-binding result for the free energy of reconstruction is 0.53 ± 0.015 eV per broken bond in the unreconstructed dislocation.

This value falls within limits placed by available experimental information and lends support to mechanisms for dislocation mobility suggested by atomistic studies [19]. In these atomistic studies, the energy re-

quired to break the reconstructed bonds in the dislocation core contributes significantly to the activation energy for dislocation mobility. The Stillinger-Weber value for the reconstruction energy, 0.81 eV, however, is too high in that it leads to a prediction [18] for the dislocation mobility which is multiple orders of magnitude lower than observed experimentally [15]. Our value for the *free* energy includes explicitly both thermal fluctuations and bonding effects. The fact that it is significantly lower than the Stillinger-Weber value tends to increase the predicted dislocation mobility and thus lends support to the mechanisms proposed in [19]. Our lower free energy leads also to a significantly higher prediction for the equilibrium density of dangling bonds in the dislocation core. The total signal strength in electron paramagnetic resonance experiments [16], whose precise origin is difficult to interpret and may involve other defects, places an absolute upper limit of a few percent on the density of dangling bonds associated with the dislocations. Our free energy value corresponds to a dangling bond density of $\sim 0.1\%$, well below the experimental bound.

Conclusions — There is tremendous benefit in separating thermal studies of a system with highly detailed models into two parts: an exploration of phase space using a simpler coarse-grained Hamiltonian and use of a more detailed Hamiltonian to study the behavior of the system at a limited number of well-chosen points in phase space. We have seen that the approach works well for the determination of the free energies of defects from quantum-based calculations. As system size increases, the determination of such local defects is relatively stable. Global changes, such as phase transitions, in which the observable of interest is correlated with the entire system may require a different approach. A thermal, quantum mechanical description of the 30° partial dislocation core gives a free energy of reconstruction which is significantly lower than previous Stillinger-Weber values and, thus, leads to a more consistent view of dislocation mobility in silicon. Finally, the number of samples required to apply the multiscale approach to systems of approximately one hundred atoms is sufficiently low as to make its application to *ab initio* calculations attractive.

Acknowledgments

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References

- [1] J. Tersoff, *Phys. Rev. Lett.* **61**, 2879 (1988).
- [2] F. Stillinger and T. Weber, *Phys. Rev.* **B31**, 5262 (1985).
- [3] J. Tersoff, *Phys. Rev.* **B38**, 9902 (1988).
- [4] M.S. Daw and M.I. Baskes, *Phys. Rev. Lett.* **50**, 1285 (1983).
- [5] W.A. Harrison, *Surface Science*, **299-300** 290 (1994).
- [6] S. Sawada, *Vacuum*, **41**, 612 (1990).
- [7] M. Kohyama, *J. Phys.: Cond. Matt.*, **3**, 2193 (1991).
- [8] M. Krajčí and J. Hafner, *Phys. Rev. Lett.* **74**, 5100 (1995).
- [9] M.C. Payne *et al.*, *Rev. Mod. Phys.* **64**, 1045 (1992).
- [10] V. Milman, *et al. Phys. Rev. Lett.* **70**, 2928 (1993).
- [11] L. Verlet *Phys. Rev.*, **159**, 98 (1967).
- [12] Metropolis *et al.*, *J. Chem. Phys.*, **21**, 1087 (1953).
- [13] J. P. Valleau and D. N. Card, *J. Comp. Phys.* **23**, 187 (1977).
- [14] J. G. Kirkwood, *J. Chem. Phys.* **3**, 300 (1935).
- [15] A. George and G. Champier, *Phys. Stat. Sol.* **A53**, 529 (1979).
- [16] H. Alexander in *Dislocations in Solids*, F.R.N. Nabarro, Ed. (Elsevier, Amsterdam, 1986), Vol. 7, Ch. 35, p. 126.
- [17] A.D. Becke, *J. Chem. Phys.*, **98**, 5648 (1993).
- [18] V.V. Bulatov, *private communication*.
- [19] V. Bulatov, S. Yip, A.S. Argon, *Phil. Mag.*, 453 (1995).

